Role of precalcination and regeneration conditions on postcombustion CO_2 capture in the Ca-looping technology

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Abstract

The Ca-looping (CaL) technology is already recognized as a potentially viable method to capture CO_2 from postcombustion gas in coal fired power plants. In this process, CO_2 is chemisorbed by CaO solid particles derived from precalcination of cheap and widely available natural limestone. The partially carbonated solids are regenerated by calcination under high CO_2 concentration. Novel CaL concepts are proposed to further improve the efficiency of the technology such as the introduction of a recarbonation reactor in between the carbonation and calcination stages to mitigate the progressive deactivation of the regenerated CaO. Process simulations aimed at retrieving optimum design parameters and operating conditions to scale-up the technology yield results critically dependent on the multicyclic sorbent performance. Nevertheless, technical limitations usually preclude lab-scale tests from mimicking realistic CaL conditions necessarily involving high CO_2 concentration for sorbent regeneration and quick transitions between carbonation and calcination. In this work, a lab-scale experimental analysis is reported on the CaO multicyclic conversion at CaL conditions closely resembling those to be expected in practice. The results presented evidence a relevant role of precalcination conditions. Precalcination in air leads to a strongly adverse effect on the activity of the sorbent regenerated under high CO_2 concentration, which is further hindered if a recarbonation stage is introduced. On the other hand, sorbent deactivation is mitigated if precalcination is carried out at conditions similar to those used for sorbent regeneration. In this case, recarbonation helps lessening the loss of multicyclic conversion, which is further enhanced by the synergistic combination with heat pretreatment. Moreover, the present study shows that the kinetics of carbonation is strongly dependent on precalcination and regeneration conditions. The diffusion controlled carbonation phase and recarbonation are intensified if the sorbent is precalcined and

regenerated under high CO_2 concentration whereas the reaction controlled carbonation phase is notably hampered.

1. INTRODUCTION

The Ca-looping (CaL) technology has recently emerged as a potentially feasible method for postcombustion CO_2 capture in coal fired power plants [1–3]. The process is based on the multicyclic carbonation/calcination of CaO. CO_2 present in the high velocity postcombustion gas stream (in a concentration of around 15% vol.) is captured by carbonation on the surface of CaO particles in a fluidized bed reactor (carbonator) operated at temperatures around 650°C under atmospheric pressure. This temperature ensures a sufficiently low value of the equilibrium CO_2 concentration ($\simeq$ 1% [4]) and, at the same time, a quick enough reaction kinetics for carbonation to occur in short residence times to considerably reduce the CO_2 concentration of the gas exiting the carbonator. The partially carbonated particles are then circulated into a second reactor (calciner) in which CaO is regenerated by calcination at high temperature while a stream of highly concentrated CO_2 gas exits the calciner ready to be compressed and transported. A critical issue of the technology is that the sorbent must be necessarily regenerated in the calciner under high CO_2 concentration (typically between 70% and 90% vol.), which requires raising up the temperature in this reactor to a value close to 950°C in order to achieve complete decarbonation in short residence times [3, 5–8]. The most feasible method to attain such high temperatures is to burn fuel in the calciner with pure oxygen (oxycombustion) for avoiding CO_2 dilution [3].

A main advantage to ensure the industrial competitiveness of the CaL technology is the low cost and wide availability of natural limestone to be employed as CaO precursor

[9, 10]. However, the multicyclic conversion of CaO derived from natural limestone decays progressively with the carbonation/calcination cycle number [11]. Lab-scale experiments show that the multicyclic conversion in short residence times of raw limestone derived CaO can be generally described by the semi-empirical equation [11–13]

$$\frac{X_N}{X_1} = \frac{X_r}{X_1} + \left[\frac{1}{k(N-1) + (1 - X_r/X_1)^{-1}}\right]; \quad (N = 1, 2...) \tag{1}$$

In Eq. 1, N is the cycle number, X_1 is CaO conversion in the 1st cycle, k is a deactivation constant and X_r is the so-called residual conversion, which is approached after a very large number of cycles. Most of data obtained for a diversity of natural limestones subjected to a wide diversity of conditions is reasonably well fitted by Eq. 1 using a residual conversion between 0.07 and 0.08 and a deactivation constant k close to 0.5 [12, 14]. Conversion of CaO derived by limestone precalcination in air is very high. Thus, in the original derivation of Eq. 1 it was assumed $X_1 \approx 1$ [12]. On the other hand, it must be remarked that CaO regeneration in lab-scale tests is usually carried out by calcination under low CO_2 concentration.

A typical run in pilot plants to validate the CaL technology is initiated by precalcining a batch of limestone in air [3]. During this period, the net production of CO_2 in the calciner is only due to decarbonation of the initial inventory of limestone [3]. Once precalcination is finished, the calciner is started to operate in the oxycombustion mode, which raises its temperature and the CO_2 concentration to a high level for continuous operation. The calcined solids are taken to the carbonator after which they are circulated back into the calciner wherein CaO regeneration would occur under high temperature/high CO_2 concentration. During continuous operation it is necessary to periodically feed the calciner with a make-up flow of fresh limestone to compensate for sorbent deactivation and loss of fine particles

generated by attrition [3, 15]. A major cause of process inefficiency is the large make up flow of fresh limestone required, which is somewhat compensated by the low cost of natural limestone and the possibility of using deactivated CaO for desulphurization and the cement industry [16, 17]. Nevertheless, it is recognized that the excessively high consumption of fuel and oxygen used to raise the calciner temperature up to high enough values for complete calcination imposes an important energy penalty to the technology [6, 18–20].

The introduction of a short recarbonation stage under high CO_2 concentration and high temperature in between the carbonator and the calciner is at the basis of a novel CaL concept aimed at minimizing the need of a large make up flow of fresh limestone to counteract sorbent deactivation [21–24]. The method is based on the recarbonation of the partially carbonated particles exiting the carbonator reactor using a high CO_2 concentration gas stream available from the calciner (see Fig. 1). Multicyclic carbonation/recarbonation/calcination thermogravimetric analysis (TGA) tests have already demonstrated that the residual conversion of raw limestone may be increased up to $X_r \simeq 0.16$ as compared to $X_r \simeq 0.07$ derived from ordinary carbonation/calcination cycles [21, 23, 25]. It is thus envisaged that the incorporation of a recarbonator reactor to the ordinary CaL process would serve to boost its efficiency by drastically reducing the required makeup flow of fresh limestone and hence the heat demand in the calciner thus lowering the overall cost of the CaL technology [21–23]. Based on these lab-scale results, a recarbonator reactor has been designed and the optimum operating conditions have been assessed [24] to validate the concept in an existing large-scale CaL pilot plant (1.7 MWth) [3] under the framework of a EU funded project (http://recal-project.eu/). Further TGA tests have shown that the sorbent performance can be additionally improved by the synergistic combination of heat pretreatment and recarbonation, which allows achieving a high and stable conversion around $X_r \simeq 0.3$ [26]. However,

it must be noticed that in the TGA tests carried out in all these works, the sorbent is pre-calcined and regenerated by calcination under a low CO_2 concentration environment. Since adding a recarbonator to the process will increase the cost and complexity of the technology, it would be important to assess the efficiency of recarbonation on the sorbent performance by means of lab-scale tests carried out at precalcination and regeneration conditions close to those to be found in practice, which necessarily involve a high CO_2 concentration.

Process simulations [2, 18, 27, 28] evidence an extraordinary sensitivity of the predicted CaL process efficiency on the CaO multicyclic conversion behavior, which emphasizes the importance of carrying out lab-scale experiments at realistic conditions for sorbent regeneration and precalcination of the makeup flow of fresh limestone. In the present manuscript, the role of precalcination and regeneration conditions on the CO_2 capture capacity of limestone derived CaO will be analyzed by means of TGA multicyclic tests. Even though a number of experimental works have shown clear evidences pointing towards a very poor carbonation reactivity of CaO derived from calcination under high CO_2 concentration [7, 29–31], technical limitations make difficult to analyze quantitatively the effect of sorbent regeneration at high temperature/high CO_2 partial pressure by means of multicyclic TGA tests. To accomplish this goal, the transition between the carbonation and calcination stages must be very short. Process simulations [15, 32] show that the solids entering the calciner to be regenerated would be heated up to the target temperature in just a few seconds. However, too low heating rates of common TG furnaces lead to excessively long transitions between the carbonation and calcination stages [29] not representative of the real process. On the other hand, the use of TG analyzers based on infrared heating allows varying the temperature at a very fast and controlled rate, which serves to shorten the transition between the carbonation and calcination stages to tens of seconds [33, 34]. Using this equipment, it has

been shown in previous works that the multicyclic performance of limestones precalcined in air is severely hampered if regeneration is carried out under high CO_2 concentration [33, 34]. Moreover, it was seen that recarbonation actually leaded in these conditions to an adverse effect on the sorbent reactivity further intensifying its drastic deactivation in the first cycles. In practical postcombustion CO_2 capture applications, only the initial batch of limestone would be precalcined in air whereas precalcination of the makeup flow of fresh limestone periodically introduced in the calciner takes place under high CO_2 concentration [3]. A pending question is whether these solids precalcined under high CO_2 concentration might exhibit a lower deactivation rate (as seen for heat pretreated limestones [11, 35, 36]), which would contribute to sustain the capture efficiency observed in pilot plants [3]. This may be a critical issue since most of the innovations proposed to improve the efficiency of the CaL technology are aimed at reducing the makeup flow of fresh limestone. The focus of the present work is to investigate the role of precalcination and sorbent regeneration conditions on the multicyclic CO_2 capture performance of limestone and how this performance is affected by recarbonation.

2. MATERIALS AND METHODS

A high purity natural limestone ($CaCO_3$ 99.62%, $SiO_2 < 0.05\%$, $Al_2O_3 < 0.05\%$, MgO 0.24%, Na_2O 0.08%) has been employed as received from Matagallar quarry (Pedrera, Spain). Limestone samples were subjected to carbonation/calcination (c/c) and carbonation/recarbonation/calcination (c/r/c) cycles using a Q5000IR TG analyzer from TA Instruments. This instrument is equipped with a furnace heated by infrared halogen lamps and a high sensitivity balance (<0.1 μg) with a minimum baseline dynamic drift (<10 μg). Infrared heating allows for very fast and controlled heating/cooling rates (300°C min^{-1})

with a rather stable change of temperature ($< \pm 4$°C).

A c/c cycle consisted of 5 min carbonation at 650°C (85% air/15% CO_2 vol/vol) followed by 5 min calcination. Benchmark calcination conditions were 70% CO_2/30% air vol/vol at 950°C. Further tests in which the sorbent was regenerated by calcination at reduced temperatures (925°C and 900°C) and in air (at 850°C) were carried out. In c/r/c cycles a 3 min recarbonation stage (10% air/90% CO_2 vol/vol) at 800°C was introduced in between the carbonation and calcination stages. A main goal of this work was to analyze the influence of precalcination conditions on the CaO multicyclic conversion. To this end, the samples were subjected in-situ to different precalcination programs. Some limestone samples were heated in air at a slow rate (20°C/min) up to 850°C, which replicates precalcination of the initial batch of limestone in the practical application. In other tests, the samples were heated under high CO_2 partial pressure (70% CO_2/30% air vol/vol) up to 950°C at a fast rate (300°C/min), which is intended to mimic precalcination of the fresh makeup flow of limestone periodically introduced in the calciner at practice to compensate for sorbent losses and deactivation. The effect of heat pretreatment as affected by precalcination and regeneration conditions has been also analyzed. For this purpose, some limestone samples were isothermally preheated in a muffle furnace at 950°C for 12 h in air, after which they were immediately carried out to the TG analyzer for testing.

In order to avoid mass transfer effects a fixed sample mass of 10 mg was employed in all the runs. As demonstrated elsewhere [37] from results derived from four different TG analyzers (including the Q5000IR used in this study) the undesired influence of diffusion resistance through the sample on the reaction rate can be disregarded for sample masses around this value. Furthermore, a small particle size (9.5 μm volume weighted mean particle size) has been selected in order to neglect intra-particle diffusion resistance, which would

be remarkable only for particle sizes larger than 300 μm [4, 38]. Finally, by using a small gas flow rate (100 cm^3min^{-1}) any possible influence of the superficial gas velocity over the sample on the reaction kinetics can be dismissed.

3. RESULTS AND DISCUSSION

3.1. Role of precalcination conditions

Multicyclic CaO conversion data retrieved from c/c tests performed on raw limestone samples are plotted in Fig. 2a (carbonation at 650°C for 5 min under 15% CO_2/85% air vol/vol and calcination for 5 min at 950°C under 70% CO_2/30% air vol/vol). The only difference between both tests regards the precalcination conditions. In order to check for repeatability, different tests were carried out under the same conditions. CaO conversion error bars are within symbol size. As can be seen in Fig. 2a, CaO resulting from quickly precalcining limestone under high CO_2 concentration shows a lower conversion in the 1st cycle ($X_1 = 0.48$) as compared to the sorbent derived from slow precalcination in air ($X_1 = 0.73$). Importantly, Fig. 2a shows also that precalcination conditions do have a determining influence on the subsequent multicyclic CaO conversion behavior. Thus, the sample precalcined in air exhibits a drastic drop of conversion after the 1st cycle, which is decreased down to a value close to 0.05 in just a few cycles as reported in a previous work [33]. In contrast, CaO conversion of the sample precalcined under high CO_2 concentration decays at a comparatively much lower rate and, after 20 cycles, it triples the value of conversion for the sample precalcined in air. Moreover, CaO conversion data for the sample precalcined under high CO_2 concentration may be well fitted by Eq. 1 (see Fig. 2a) yielding a residual value of conversion $X_r \simeq 0.079$ similar to the residual conversion reported for sorbents precalcined

and regenerated under low CO_2 partial pressure [12]. Yet, Eq. 1 does not provide a good fit to CaO conversion data for the sorbent precalcined in air and regenerated under high CO_2 concentration. In this case, CaO conversion is just characterized by a drastic drop in the first cycles to rapidly approach a very small residual value.

The thermograms shown in Fig. 2b illustrate some distinctive features that help explaining the determining effect of precalcination conditions on the multicyclic conversion of CaO regenerated under high CO_2 concentration. As well known from previous studies [38, 39], the carbonation stage is seen to take place through two different phases. A first reaction controlled phase takes place on the exposed surface of the CaO particles, which is followed by a relatively slower phase controlled by diffusion of CO_3^{2-} mobile ions and counter-current diffusion of O^{2-} anions through the $CaCO_3$ product layer [40, 41]. Once the 5 min carbonation stage is finished, the CO_2 vol.% is suddenly increased up to 70% and the temperature is increased up to 950°C at a rate of 300°C/min. Accidental recarbonation occurs then until the temperature reaches a sufficiently high value (around 870°C) to reverse the reaction, which is reflected by the sharp weight gain observed in this transitory period of tens of seconds (see Fig. 2b). Another interesting feature observed in Fig. 2b is that the sorbent resulting from precalcination in air shows a much higher reactivity in the fast carbonation phase of the 1st cycle ($N = 1$ in Fig. 2b) as compared to CaO derived from precalcination under high CO_2 concentration. This result may be explained from the enhancement of CaO sintering by precalcination under high CO_2 concentration as well reported in the literature [42, 43], which leads to a reduction of the CaO surface area available for reaction. On the other hand, the drastic drop of conversion in the first cycles exhibited by the sorbent regenerated under high CO_2 concentration and precalcined in air would be indicative of a high susceptibility of the CaO skeleton resulting for precalcination in air to sintering. A

further phenomenon that might play a role on this severe loss of CaO reactivity would be the preferential growth of the regenerated CaO surface along crystallographic planes wherein carbonation would be energetically unfavorable according to ab-initio theoretical works [44] been though this hypothesis has not been confirmed by experimental observations yet. In regards to the diffusion controlled carbonation phase, Fig. 2b shows that it is intensified by precalcination under high CO_2 concentration. Diffusion controlled carbonation is also promoted for the sorbent precalcined in air from the 2nd cycle after being regenerated under high CO_2 concentration in the 1st cycle. As seen in the inset of Fig. 2b, diffusion controlled carbonation represents a relevant contribution to the overall CaO conversion in the 5 min carbonation stage for the last cycles and it is particularly relevant for the sample precalcined under high CO_2 concentration.

3.2. Role of precalcination conditions on the effect of recarbonation

Next the influence of precalcination conditions on the effect of an intentionally introduced recarbonation stage (as proposed in the novel CaL concept [21, 23, 24] to reactivate the sorbent) will be analyzed. Multicyclic CaO conversion data retrieved from c/r/c tests are plotted in Fig. 3a along with data shown above from c/c tests. Remarkably, it is observed that the effect of recarbonation is essentially dependent upon the conditions of precalcination. The data shows that introducing on purpose a recarbonation stage would be detrimental at realistic sorbent regeneration conditions if precalcination is carried out in air. Under these conditions, the introduction of a recarbonation stage intensifies even further the severe drop of conversion to a value of only around 0.04 in just a few cycles. Conversely, if precalcination is carried out under high CO_2 concentration, recarbonation enhances the reactivity of the regenerated sorbent. Multicyclic conversion data is, in this case, well fitted

by Eq. 1 yielding a residual conversion $X_r \simeq 0.131$, which is substantially higher than the residual conversion derived from c/c tests under the same precalcination and regeneration conditions ($X_r \simeq 0.079$).

Thermograms obtained from c/r/c tests are depicted in Fig. 3b. As may be seen, diffusion controlled carbonation and recarbonation in the 1st cycle is more marked for the sample precalcined under high CO_2 concentration. On the other hand, the carbonation reactivity of the sample precalcined in air is severely reduced after a few cycles both in the fast and diffusion controlled phases of the carbonation stage. Yet, its carbonation reactivity in the recarbonation stage is kept at a high level being it notably enhanced after the 1st cycle as compared to the sample precalcined under high CO_2 concentration. According to a recently proposed mechanism for product layer formation and growth, $CaCO_3$ would nucleate on the CaO surface in islands with a critical size determined by temperature controlled surface diffusion [45, 46]. Since surface diffusion becomes significant at temperatures close to the Huttig temperature ($T_H \simeq 690$°C for CaO and $T_H \simeq 260$°C for $CaCO_3$ [47]), it would be greatly enhanced when the temperature is increased up to 800°C for recarbonation. The intense recarbonation observed would be thus indicative of a high surface diffusion controlled reactivity at this high temperature/high CO_2 concentration (800°C, 90% vol CO_2) even though the reactivity in the kinetically controlled fast carbonation phase (at 650°C/15% vol CO_2) stays very low.

3.3. Role of precalcination conditions on the effect of heat pretreatment

In this section the effect of heat pretreatment (isothermal preheating in air at 950°C for 12h) as determined by precalcination conditions will be analyzed. Thermograms derived from c/r/c tests carried out on heat pretreated limestone samples are shown in Fig. 4. As

inferred from previous tests on raw limestone it is also observed that the sample precalcined in air suffers a marked drop of reactivity in the carbonation stage after regeneration under high CO_2 concentration, even though the activity in the diffusion controlled recarbonation stage is rather intense. On the other hand, a remarkable reactivation in the carbonation stage is observed for the 2nd cycle if the heat pretreated sorbent is precalcined under high CO_2 concentration. As seen in Fig. 4, during precalcination under high CO_2 concentration there is sharp peak in the weight gain caused by fast carbonation/decarbonation of the heat pretreated sorbent. Heat pretreatment leads then to increased values of CaO conversion in the carbonation stage from the 2nd cycle for a large number of cycles as compared with raw limestone.

Multicyclic CaO conversion data obtained for heat pretreated samples are plotted in Fig. 5. As may be seen, heat pretreatment does not yield reactivation in c/c tests and conversion after the 1st cycle is kept at a small value when precalcined under high CO_2 concentration. In these conditions, conversion data can be well fitted by Eq. 1 with a similar value of residual conversion to that of raw limestone tested under the same conditions, although conversion of the heat pretreated sample in the 1st cycle is very small ($X_r \simeq 0.13$). Precalcination of the heat pretreated sample in air causes a further drop of CaO conversion, which is even more intense in c/r/c tests. On the other hand, the combination of heat pretreatment, precalcination under high CO_2 concentration and recarbonation yields a remarkable reactivation of CaO conversion from the 2nd c/r/c cycle after which it is kept at a value neatly above the conversion of raw limestone subjected to c/r/c cycles under the same conditions. Thus, the synergistic combination of heat pretreatment and recarbonation leads to a positive effect on the multicyclic CaO conversion but only when precalcination and sorbent regeneration are both carried out under high CO_2 concentration.

3.4. Additional CaO conversion in the recarbonation stage

Figure 6 shows the extra CaO conversion suffered by the sorbent in the recarbonation stage (ΔX) as a function of the c/r/c cycle number for heat pretreated and raw limestone samples precalcined under different conditions and regenerated under high CO_2 concentration. Data from c/r/c tests in which precalcination and regeneration were carried out in air (reported in a previous work [26]) are plotted for comparison. As was inferred from the thermograms seen in Fig. 2, the reactivity of the sorbent in the recarbonation stage is not remarkable for the raw limestone precalcined in air. It becomes however intense in the 2nd cycle after regeneration under high CO_2 concentration after which it decreases progressively with the cycle number approximately conforming to a potential law. Conversion in the recarbonation stage exhibits a similar decrease for the heat pretreated sample precalcined and regenerated in air although the values of ΔX in these conditions are comparatively much smaller. On the other hand, ΔX shows a qualitatively different trend with the cycle number for the raw and heat pretreated samples precalcined under high CO_2 concentration. As can be seen in Fig. 6, ΔX reaches a high and stable value for these samples after about 10 cycles and even increases slightly after 15 cycles.

Regardless of precalcination conditions, heat pretreatment leads to a net increase of ΔX, which indicates that the effect of the intense thermal stresses generated during heat pretreatment in the solid structure that favor diffusion [48] (and therefore accelerate recarbonation) remain in the solid structure after cycling. Likewise, diffusion is promoted by regeneration under high CO_2 concentration but precalcination in air leads to a long term progressive loss of activity in the diffusion controlled recarbonation stage. Thus, the sorbent derived from precalcination in air would have an initial high activity but would be also more susceptible

to sintering by lattice diffusion during regeneration under high CO_2 concentration, which would cause an abrupt drop of the reactive surface area available for fast carbonation and a progressive loss of activity in the recarbonation stage. Moreover, the intensification of carbonation in the recarbonation stage would contribute to further promote sintering of the regenerated porous skeleton upon calcination under high CO_2 concentration. If recarbonation is, on the other hand, carried out on the sorbent resulting from precalcination under high CO_2 concentration, the CaO skeleton resulting from regeneration would be provided with a higher stability to mitigate sintering and loss of reactivity in the carbonation stage. As seen in Fig. 6, ΔX for the raw limestone precalcined and regenerated under high CO_2 concentration reaches a rather high value ($\Delta X \gtrsim 0.13$ after 20 cycles) as compared with the values reported elsewhere (residually $\Delta X_r \simeq 0.04$ [21, 23]) from c/r/c tests in which precalcination and regeneration was performed in air and for similar carbonation/recarbonation conditions. As seen in Fig. 6 small values of ΔX are also reproducible from the tests presented in this work if precalcination and regeneration are carried out in air (it is obtained obtain $\Delta X \simeq 0.06$ after 20 cycles and it keeps decreasing).

For practical purposes, Fig. 6 reveals clearly that only if precalcination and sorbent regeneration are carried out under high CO_2 concentration, a stable value of extra conversion in the recarbonator ΔX can be assumed, which is considerably large for raw limestone ($\Delta X \gtrsim 0.15$ after 20 cycles) and even greater for the heat pretreated limestone ($\Delta X \gtrsim 0.15$ after 20 cycles) as compared with the extra conversion exhibited by the sample precalcined and regenerated in air. Moreover, ΔX shows a tendency to increase slightly with the cycle number. To further remark this issue, the time evolution of conversion during the 20th c/r/c cycle is plotted in Fig. 7 for raw limestone. This figure reveals another relevant feature concerning the kinetics of carbonation and recarbonation as determined by precalcination

and sorbent regeneration conditions. As may be seen, the time evolution of conversion in both carbonation and recarbonation stages conforms to the generally accepted picture of a fast kinetically driven carbonation phase well differentiated from a subsequent diffusion controlled slower phase. For the sorbent precalcined and regenerated in air, conversion in this slow phase is negligibly small as compared to conversion in the fast phase. This scenario has been usually assumed for the design of efficient scaled-up carbonator reactors [2]. It is also observed that, under these conditions, conversion in the recarbonation stage is comparatively very small as discussed above, which has been also assumed for the design of a recarbonator reactor based on a bubbling fluidized bed [24]. It is seen however that realistic regeneration conditions (as regards a high CO_2 partial pressure in the calciner) leads to a quite diverse scenario. In this case, the fast phase in the carbonation stage is extremely limited whereas the subsequent diffusion controlled phase is enhanced. On the other hand, the kinetics of carbonation in the recarbonation stage is also notably promoted, which may be explained from the intensification of diffusion caused by regeneration under high temperature/high CO_2 concentration. The highly adverse effect of precalcination in air and regeneration under high CO_2 concentration on the sorbent performance is specially marked in the kinetically controlled fast phase as seen in Fig. 7 (conversion in the fast carbonation phase of the 20th cycle for the raw limestone is just 0.015 under these conditions).

3.5. SEM analysis

Scanning Electron microscopy (SEM) images of samples taken after being subjected to multicyclic tests under different precalcination and regeneration conditions may be seen in Fig. 8. As can be observed, the samples precalcined in air and regenerated under CO_2 concentration (with the lowest carbonation activity after the 20 cycles) show rather large

grains as compared with those observed for the samples precalcined and regenerated in air (with the highest carbonation activity after the cycles) whereas an intermediate grain size is seen for the samples precalcined and regenerated under high CO_2 concentration. In the latter case, the samples subjected to an intermediate recarbonation stage exhibit a smaller grain size as compared to those subjected to ordinary c/c cycles. It may be observed also that CaO grains have a characteristic size determined by the conditions of the tests with little variation around an average value. Figure 9a shows data on CaO conversion at the 20th cycle X_{21} (left axis) as a function of the average grain size d (calculated from a statistical analysis of the SEM images). As can be seen, X_{21} scales inversely proportional to d.

The necessarily small amount of sample used for the TGA tests to avoid mass transfer effects (just 10 mg) is not sufficient to obtain the BET surface area of the cycled samples by means of physisorption analysis. For typical values of the BET surface area of CaO derived from limestone calcination ($\sim$ 1 - 10 m^2/g) [49], a sample mass between 200 and 300 mg is needed to retrieve reliable results from this technique [50]. However, a rough estimation of the specific surface area may be obtained from the average CaO grain size d as $S_d = 6/(\rho_{CaO} d)$, where $\rho_{CaO} \simeq 3.37$ g/cm^3 is the CaO solid density. The calculated values of S_d in this way (Fig. 9b, right axis), which are in the range between $\sim$ 2 and 15 m^2/g, conform to the typical BET values reported for CaO samples derived from natural limestone calcination under diverse atmospheres and temperatures [49]. Thus, S_d can be taken as an acceptable measure to quantify the effect of the tests conditions on the CaO surface area. The observed scaling of CaO conversion with the average grain size ($X_{21} \propto 1/d$, Fig. 9a) suggests therefore that the carbonation reactivity of the cycled CaO is mainly determined by the surface area available for reaction ($X \propto S_d$) as assumed in previous works [2, 11, 51].

The thickness of the $CaCO_3$ product layer that marks the end of the reaction-controlled

carbonation phase on the surface of the CaO particles is between 30 and 50 nm [38–40], which is smaller that the typical size of the pores inferred from the SEM images of the cycled samples under high CO_2 concentration. Thus, by assuming that the reaction surface is flat, CaO conversion in the fast phase can be approximately calculated [2, 51] as

$$X = \left[\frac{M_{CaO}}{M_{CaCO3}} \rho_{\mathrm{CaCO3}} h \right] S \tag{2}$$

where M_{CaO}/M_{CaCO3} is the ratio of $CaO/CaCO_3$ molecular weights and $\rho_{CaCO3} = 2.71$ g/cm^3 is the $CaCO_3$ solid density. Measured data of CaO conversion at the 20th cycle of the tests are plotted in Fig. 9b versus the predicted values from Eq. 2 using $S = S_d$ and $h = 40$ nm. As may be seen, the measured values of conversion are just about a 30% of those predicted by Eq. 2, which suggests that the reactivity of the cycled CaO is not just hampered by surface area reduction. Moreover, it must be taken into account that the measured values are augmented by the contribution of the nonnegligible diffusion controlled phase in the 5 min carbonation period. A proposed mechanism that may extraordinarily hinder the cycled CaO reactivity is the preferential growth of the regenerated CaO exposed surface along crystallographic planes wherein carbonation would be energetically unfavorable [44] even though this hypothesis has not been experimentally validated yet.

A further aspect to be assessed for the use of natural limestone in the CaL technology is the likely fragmentation of the particles when subjected to intense mechanical and thermal stresses. Thermal stresses would be enhanced by regeneration under realistic calcination conditions and the fast changes of temperature caused by rapid transitions between stages. Regardless of the loss of CaO reactivity, high attrition rates would require a makeup of fresh sorbent in order to compensate for material losses by elutriation of very fine fragments [1, 30]. In the SEM analysis of the present work clear evidences were observed of significant

fragmentation after the samples were cycled under certain conditions as illustrated in Fig. 10. Similarly to the effect of recarbonation on sorbent reactivity, SEM images suggest that the effect of recarbonation on the friability of the sorbent will depend on the conditions of precalcination. As seen in Fig. 10, some particles of the samples precalcined in air and subjected to an intermediate recarbonation stage appear markedly fractured as well as those of the sample precalcined under high temperature/high CO_2 concentration but not subjected to recarbonation. These observations indicate that, from the point of view of minimizing fragmentation, recarbonation will be beneficial if the sorbent is precalcined under high CO_2 concentration but it would be detrimental if the solids are precalcined in air, which is in close analogy with the effect of recarbonation on CaO reactivity.

Finally, it must be remarked that, besides of the high CO_2 concentration in the calciner investigated in the present work, other sources of sorbent deactivation are expected to play a role in the practical application such as irreversible sulphation caused by the presence of SO_2 not only in the flue gas but also in the calciner as produced by oxycombustion [52]. Since sulphation is mainly limited by pore blocking [53], it is foreseeable that the enhancement of CaO sintering as due to regeneration under CO_2 might contribute to enhance it, which would intensify further the loss of CaO carbonation reactivity. A study of the sorbent multicyclic performance as affected by the simultaneous presence of CO_2 and SO_2 will be the subject of a separate work.

4. CONCLUSIONS

A main conclusion is that although CaO derived from limestone precalcination in air shows a high carbonation activity in the reaction-controlled fast phase, it is prone to suffer a drastic deactivation after being regenerated under high CO_2 concentration as must be

necessarily in the CaL technology for CO_2 postcombustion capture. In contrast, CaO derived from limestone precalcination under high CO_2 concentration exhibits a relatively lower reactivity but, on the other hand, its deactivation after being regenerated under high CO_2 concentration is mitigated. Most of carbonation in short residence times takes place in the fast kinetically controlled phase when sorbent regeneration is carried out in air. However, if the sorbent is regenerated under realistic conditions involving high CO_2 concentration, carbonation in the fast phase is severely hindered whereas diffusion-controlled carbonation is notably enhanced and represents a significant contribution to CO_2 capture for residence times of the order of minutes.

The most favorable scenario to enhance CaO conversion in the carbonation stage under realistic regeneration conditions is seen when heat pretreatment, recarbonation and (importantly) precalcination under high CO_2 concentration are combined. By means of this synergistic combination, the value of CaO conversion retrieved from the tests after 20 cycles is around 0.19. If precalcination is carried out in air, this value falls drastically to just 0.04. Furthermore, SEM images of samples precalcined in air and regenerated under high CO_2 concentration demonstrate clear evidences of particle fragmentation, which suggests that, besides of the decreased CaO reactivity, considerable material losses may be expected at these conditions as due to the generation of fine particles. On the other hand, particle fragmentation has not been observed if precalcination is carried out under high CO_2 concentration and a recarbonation stage is introduced.

In regards to the novel CaL concept based on the introduction of a recarbonation stage, optimum design parameters for efficient recarbonator reactors have been estimated elsewhere on the basis of a targeted extra conversion in the recarbonator ΔX $\simeq$0.02-0.04 and a residual CaO conversion in the carbonator X_r $\simeq$0.16-0.17 (derived from tests on raw limestone

precalcined and regenerated in air and subjected to carbonation/recarbonation/calcination cycles). The present study shows that more realistic values would be $\Delta X \sim X_r \simeq 0.13$ for raw limestone precalcined and regenerated under high CO_2 concentration. The considerable increase of conversion in the recarbonator under realistic regeneration conditions would entail an increase of heat demand in the calciner since the solids entering it would have a higher carbonate content. However, the enhancement of recarbonation might allow decreasing the temperature of the recarbonator while still achieving a substantial increment of residual conversion in the carbonation stage, which would reduce the energy penalty associated to the possible need of heating up the recarbonator reactor to attain a high enough recarbonation efficiency.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

[1] J. Blamey, E. J. Anthony, J. Wang, and P. S. Fennell, "The calcium looping cycle for large-scale CO_2 capture," *Prog. Energ. Combust. Sci.*, vol. 36, no. 2, pp. 260–279, 2010.

[2] M. C. Romano, "Modeling the carbonator of a Ca-looping process for CO_2 capture from power plant flue gas," *Chemical Engineering Science*, vol. 69, pp. 257 – 269, 2012.

[3] B. Arias, M. Diego, J. Abanades, M. Lorenzo, L. Diaz, D. Martinez, J. Alvarez, and A. Sanchez-Biezma, "Demonstration of steady state CO_2 capture in a 1.7 MWth calcium looping pilot," *International Journal of Greenhouse Gas Control*, vol. 18, pp. 237–245, 2013.

[4] F. Garcia-Labiano, A. Abad, L. de Diego, P. Gayan, and J. Adanez, "Calcination of calcium-based sorbents at pressure in a broad range of CO_2 concentrations," *Chemical Engineering Science*, vol. 57, no. 13, pp. 2381 – 2393, 2002.

[5] A. Charitos, N. Rodriguez, C. Hawthorne, M. Alonso, M. Zieba, B. Arias, G. Kopanakis, G. Scheffknecht, and J. C. Abanades, "Experimental validation of the Calcium Looping CO_2 capture process with two circulating fluidized bed carbonator reactors," *Industrial & Engineering Chemistry Research*, vol. 50, no. 16, pp. 9685–9695, 2011.

[6] I. Martinez, G. Grasa, R. Murillo, B. Arias, and J. Abanades, "Modelling the continuous calcination of $CaCO_3$ in a Ca-looping system," *Chemical Engineering Journal*, vol. 215–216, pp. 174–181, 2013.

[7] R. T. Symonds, D. Y. Lu, V. Manovic, and E. J. Anthony, "Pilot-scale study of CO_2 capture by cao-based sorbents in the presence of steam and SO_2," *Industrial & Engineering Chemistry Research*, vol. 51, no. 21, pp. 7177 – 7184, 2012.

[8] A. Coppola, F. Scala, P. Salatino, and F. Montagnaro, "Fluidized bed calcium looping cycles for CO_2 capture under oxy-firing calcination conditions: Part 1. assessment of six limestones," *Chemical Engineering Journal*, vol. 231, pp. 537 – 543, 2013.

[9] M. C. Romano, I. Martinez, R. Murillo, B. Arstad, R. Blom, D. C. Ozcan, H. Ahn, and S. Brandani, "Process simulation of Ca-looping processes: review and guidelines," *Energy Procedia*, vol. 37, pp. 142 – 150, 2013.

[10] M.-H. Chang, C.-M. Huang, W.-H. Liu, W.-C. Chen, J.-Y. Cheng, W. Chen, T.-W. Wen, S. Ouyang, C.-H. Shen, and H.-W. Hsu, "Design and experimental investigation of Calcium Looping process for 3-kWth and 1.9-MWth facilities," *Chemical Engineering & Technology*, vol. 36, no. 9, pp. 1525–1532, 2013.

[11] J. M. Valverde, "A model on the CaO multicyclic conversion in the Ca-looping process," *Chemical Engineering Journal*, vol. 228, pp. 1195–1206, 2013.

[12] G. S. Grasa and J. C. Abanades, "CO_2 capture capacity of CaO in long series of carbonation/calcination cycles," *Ind. Eng. Chem. Res.*, vol. 45, no. 26, pp. 8846–8851, 2006.

[13] J. M. Valverde, P. E. Sanchez Jimenez, A. Perejon, and L. A. Perez-Maqueda, "CO_2 multicyclic capture of pretreated/doped CaO in the Ca – looping process. Theory and experiments," *Phys. Chem. Chem. Phys.*, vol. 15, pp. 11775 – 11793, 2013.

[14] J. Wang, V. Manovic, Y. Wu, and E. J. Anthony, "A study on the activity of CaO-based sorbents for capturing CO_2 in clean energy processes," *Applied Energy*, vol. 87, no. 4, pp. 1453 – 1458, 2010.

[15] J. Ylatalo, J. Ritvanen, T. Tynjala, and T. Hyppanen, "Model based scale-up study of the calcium looping process," *Fuel*, vol. 115, pp. 329–337, 2014.

[16] A. Sanchez-Biezma, J. Ballesteros, L. Diaz, E. de Zarraga, F. Alvarez, J. Lopez, B. Arias, G. Grasa, and J. Abanades, "Postcombustion CO_2 capture with CaO. status of the technology and next steps towards large scale demonstration," *Energy Procedia*, vol. 4, no. 0, pp. 852 – 859, 2011.

[17] H. Chen, Z. Zhao, X. Huang, K. Patchigolla, A. Cotton, and J. Oakey, "Novel optimized process for utilization of CaO-based sorbent for capturing CO_2 and SO_2 sequentially," *Energy Fuels*, vol. 26, pp. 5596–5603, 2012.

[18] N. Rodriguez, M. Alonso, G. Grasa, and J. C. Abanades, "Heat requirements in a calciner of $CaCO_3$ integrated in a CO_2 capture system using CaO," *Chemical Engineering Journal*, vol. 138, no. 1–3, pp. 148–154, 2008.

[19] L. M. Romeo, Y. Lara, P. Lisbona, and J. M. Escosa, "Optimizing make-up flow in a CO_2 capture system using CaO," *Chemical Engineering Journal*, vol. 147, no. 2-3, pp. 252 – 258, 2009.

[20] A. Martinez, Y. Lara, P. Lisbona, and L. M. Romeo, "Operation of a cyclonic preheater in the Ca-looping for CO_2 capture," *Environmental Science & Technology*, vol. 47, no. 19, pp. 11335–11341, 2013.

[21] B. Arias, G. S. Grasa, M. Alonso, and J. C. Abanades, "Post - combustion calcium looping process with a highly stable sorbent activity by recarbonation," *Energy Environ. Sci.*, vol. 5, pp. 7353 – 7359, 2012.

[22] M. E. Diego, B. Arias, M. Alonso, and J. C. Abanades, "The impact of calcium sulfate and inert solids accumulation in post-combustion calcium looping systems," *Fuel*, vol. 109, pp. 184 – 190, 2013.

[23] G. Grasa, I. Martnez, M. E. Diego, and J. C. Abanades, "Determination of CaO carbonation kinetics under recarbonation conditions," *Energy & Fuels*, doi:10.1021/ef500331t.

[24] M. E. Diego, B. Arias, G. S. Grasa, and J. C. Abanades, "Design of a novel fluidized bed reactor to enhance sorbent performance in CO_2 capture systems using CaO," *Industrial & Engineering Chemistry Research*, doi:10.1021/ie500630p.

[25] J. M. Valverde, P. E. Sanchez-Jimenez, L. A. Perez-Maqueda, M. Quintanilla, and J. Perez-Vaquero, "Role of crystal structure on capture by limestone derived CaO subjected to carbonation/recarbonation/calcination cycles at Ca-looping conditions," *Applied Energy*, vol. 125, pp. 264 – 275, 2014.

[26] J. M. Valverde, P. E. Sanchez Jimenez, and L. A. Perez Maqueda, "High and stable CO_2 capture capacity of natural limestone at Ca-looping conditions by heat pretreatment and recarbonation synergy," *Fuel*, vol. 123, pp. 79–85, 2014.

[27] L. M. Romeo, Y. Lara, P. Lisbona, and A. Martinez, "Economical assessment of competitive enhanced limestones for CO_2 capture cycles in power plants," *Fuel Processing Technology*, vol. 90, no. 6, pp. 803 – 811, 2009.

[28] I. Martnez, G. Grasa, R. Murillo, B. Arias, and J. Abanades, "Modelling the continuous calcination of $CaCO_3$ in a Ca-looping system," *Chemical Engineering Journal*, vol. 215-216, pp. 174–181, 2013.

[29] D. Y. Lu, R. W. Hughes, E. J. Anthony, and V. Manovic, "Sintering and reactivity of $CaCO_3$-based sorbents for in situ CO_2 capture in fluidized beds under realistic calcination conditions," *J. Environ. Eng.*, vol. 135, no. 6, pp. 404–410, 2009.

[30] V. Manovic, J.-P. Charland, J. Blamey, P. S. Fennell, D. Y. Lu, and E. J. Anthony, "Influence of calcination conditions on carrying capacity of CaO-based sorbent in CO_2 looping cycles,"

554 *Fuel*, vol. 88, pp. 1893–1900, 2009.

555 [31] C. Luo, Y. Zheng, J. Guo, and B. Feng, "Effect of sulfation on CO_2 capture of cao-based
556 sorbents during calcium looping cycle," *Fuel*, pp. –, 2013.

557 [32] J. Ylatalo, J. Parkkinen, J. Ritvanen, T. Tynjala, and T. Hyppanen, "Modeling of the oxy-
558 combustion calciner in the post-combustion calcium looping process," *Fuel*, vol. 113, pp. 770–
559 779, 2013.

560 [33] J. M. Valverde, P. E. Sanchez-Jimenez, and L. A. Perez-Maqueda, "Calcium-looping for post-
561 combustion CO_2 capture. on the adverse effect of sorbent regeneration under CO_2," *Applied*
562 *Energy*, vol. 126, pp. 161–171, 2014.

563 [34] J. M. Valverde, P. E. Sanchez-Jimenez, and L. A. Perez-Maqueda, "Effect of heat pretreat-
564 ment/recarbonation in the Ca-looping process at realistic calcination conditions," *Energy &*
565 *Fuels*, vol. 28, no. 6, pp. 4062–4067, 2014.

566 [35] V. Manovic and E. J. Anthony, "Thermal activation of CaO-based sorbent and self-reactivation
567 during CO_2 capture looping cycles," *Environ. Sci. Technol.*, vol. 42, pp. 4170–4174, 2008.

568 [36] J. M. Valverde, P. E. Sanchez-Jimenez, A. Perejon, and L. A. Perez-Maqueda, "Constant rate
569 thermal analysis for enhancing the long-term CO_2 capture of CaO at Ca-looping conditions,"
570 *Applied Energy*, vol. 108, pp. 108 – 120, 2013.

571 [37] M. Alonso, Y. Criado, J. Abanades, and G. Grasa, "Undesired effects in the determination of
572 CO_2 carrying capacities of CaO during TG testing," *Fuel*, vol. 127, pp. 52–61, 2014.

573 [38] G. Grasa, R. Murillo, M. Alonso, and J. C. Abanades, "Application of the random pore model
574 to the carbonation cyclic reaction," *AIChE J.*, vol. 55, no. 5, pp. 1246–1255, 2009.

575 [39] R. Barker, "Reversibility of the reaction $CaCO_3$ =CaO+CO_2," *J. Appl. Chem. Biotechnol.*,
576 vol. 23, pp. 733 – 742, 1973.

[40] S. K. Bhatia and D. D. Perlmutter, "Effect of the product layer on the kinetics of the CO_2-lime reaction," *AIChE Journal*, vol. 29, no. 1, pp. 79–86, 1983.

[41] Z. Sun, S. Luo, P. Qi, and L.-S. Fan, "Ionic diffusion through calcite ($CaCO_3$) layer during the reaction of cao and CO_2," *Chemical Engineering Science*, vol. 81, pp. 164 – 168, 2012.

[42] R. H. Borgwardt, "Calcium oxide sintering in atmospheres containing water and carbon dioxide," *Industrial & Engineering Chemistry Research*, vol. 28, no. 4, pp. 493 – 500, 1989.

[43] B. Stanmore and P. Gilot, "Review - calcination and carbonation of limestone during thermal cycling for CO_2 sequestration," *Fuel Processing Technology*, vol. 86, no. 16, pp. 1707 – 1743, 2005.

[44] R. Besson and L. Favergeon, "Atomic - scale study of calcite nucleation in calcium oxide," *The Journal of Physical Chemistry C*, vol. 117, no. 17, pp. 8813 – 8821, 2013.

[45] Z.-S. Li, F. Fang, X.-Y. Tang, and N.-S. Cai, "Effect of temperature on the carbonation reaction of CaO with CO_2," *Energy & Fuels*, vol. 26, no. 4, pp. 2473–2482, 2012.

[46] Z. Li, H. Sun, and N. Cai, "Rate equation theory for the carbonation reaction of cao with CO_2," *Energy & Fuels*, vol. 26, no. 7, pp. 4607–4616, 2012.

[47] A. M. Kierzkowska, R. Pacciani, and C. R. Müller, "CaO-based CO_2 sorbents: From fundamentals to the development of new, highly effective materials," *ChemSusChem*, vol. 6, no. 7, pp. 1130–1148, 2013.

[48] J. M. Valverde, P. E. Sanchez-Jimenez, A. Perejon, and L. A. Perez-Maqueda, "Role of looping-calcination conditions on self-reactivation of thermally pretreated CO_2 sorbents based on CaO," *Energy & Fuels*, vol. 27, p. 3373 3384, 2013.

[49] C. Chen, C. Zhao, C. Liang, and K. Pang, "Calcination and sintering characteristics of limestone under O_2/CO_2 combustion atmosphere," *Fuel Processing Technology*, vol. 88, no. 2,

pp. 171 – 178, 2007.

[50] J. B. Condon, *Surface Area and Porosity Determinations by Physisorption, Measurements and Theory*. Elsevier, 1st ed., 2006.

[51] G. S. Grasa, M. Alonso, and J. C. Abanades, "Sulfation of CaO particles in a carbonation/calcination loop to capture CO_2," *Ind. Eng. Chem. Res.*, vol. 47, pp. 1630 – 1635, 2008.

[52] Y. Hu and J. Yan, "Characterization of flue gas in oxy-coal combustion processes for CO_2 capture," *Applied Energy*, vol. 90, no. 1, pp. 113 – 121, 2012.

[53] E. O'Neill, D. Keairns, and W. Kittle, "A thermogravimetric study of the sulfation of limestone and dolomitethe effect of calcination conditions," *Thermochimica Acta*, vol. 14, no. 12, pp. 209 – 220, 1976.

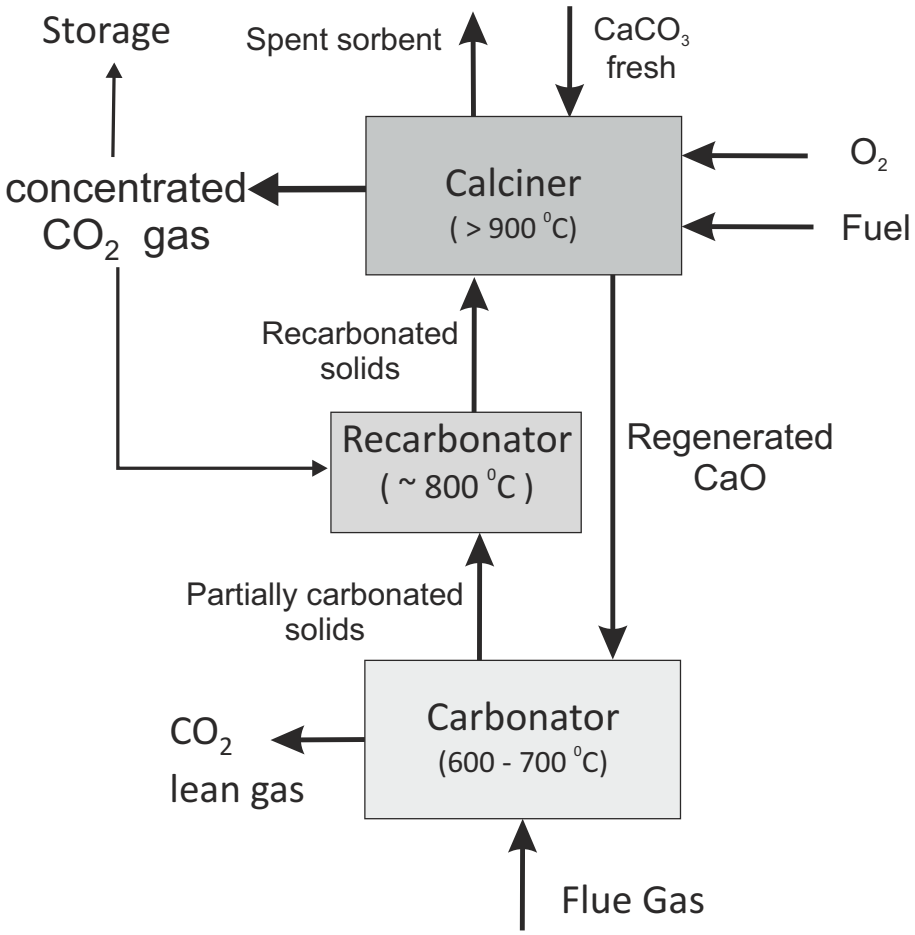


FIG. 1: Schematic representation of the Ca-looping process for post-combustion CO_2 capture modified by introducing a recarbonator reactor.

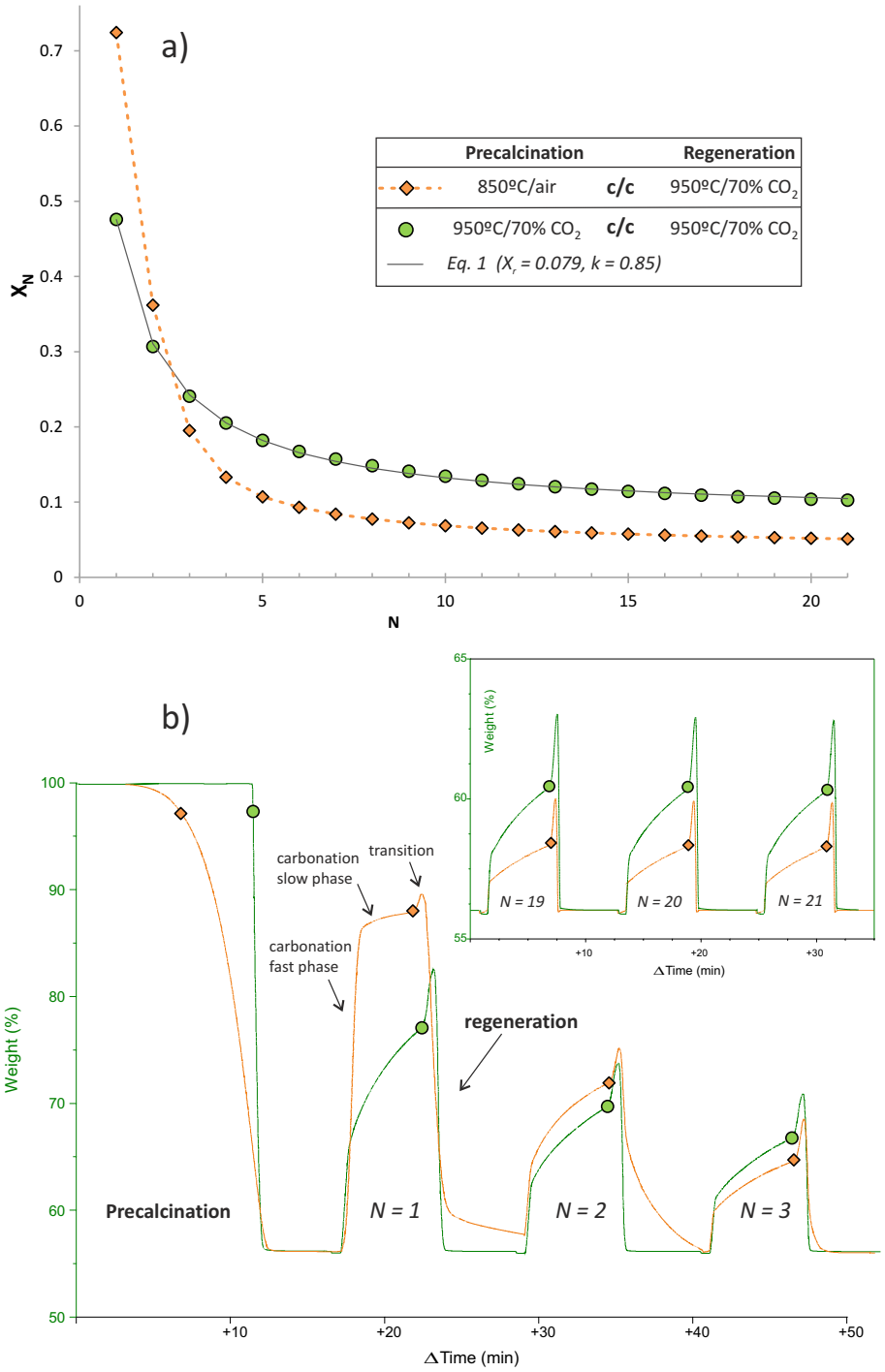


FIG. 2: a) CaO conversion at the end of the carbonation stage (X_N) as a function of the carbonation/calcination (c/c) cycle number (N) for samples of raw limestone. Carbonation at 650°C for 5 min (15% CO_2/85% air vol/vol), calcination (regeneration) for 5 min at 950°C (70% CO_2/30% air vol/vol). Different precalcination conditions are indicated. The solid line in a) is the best fit from Eq. 1. b) Time evolution of sorbent weight % during precalcination and the three first and last (inset) cycles.

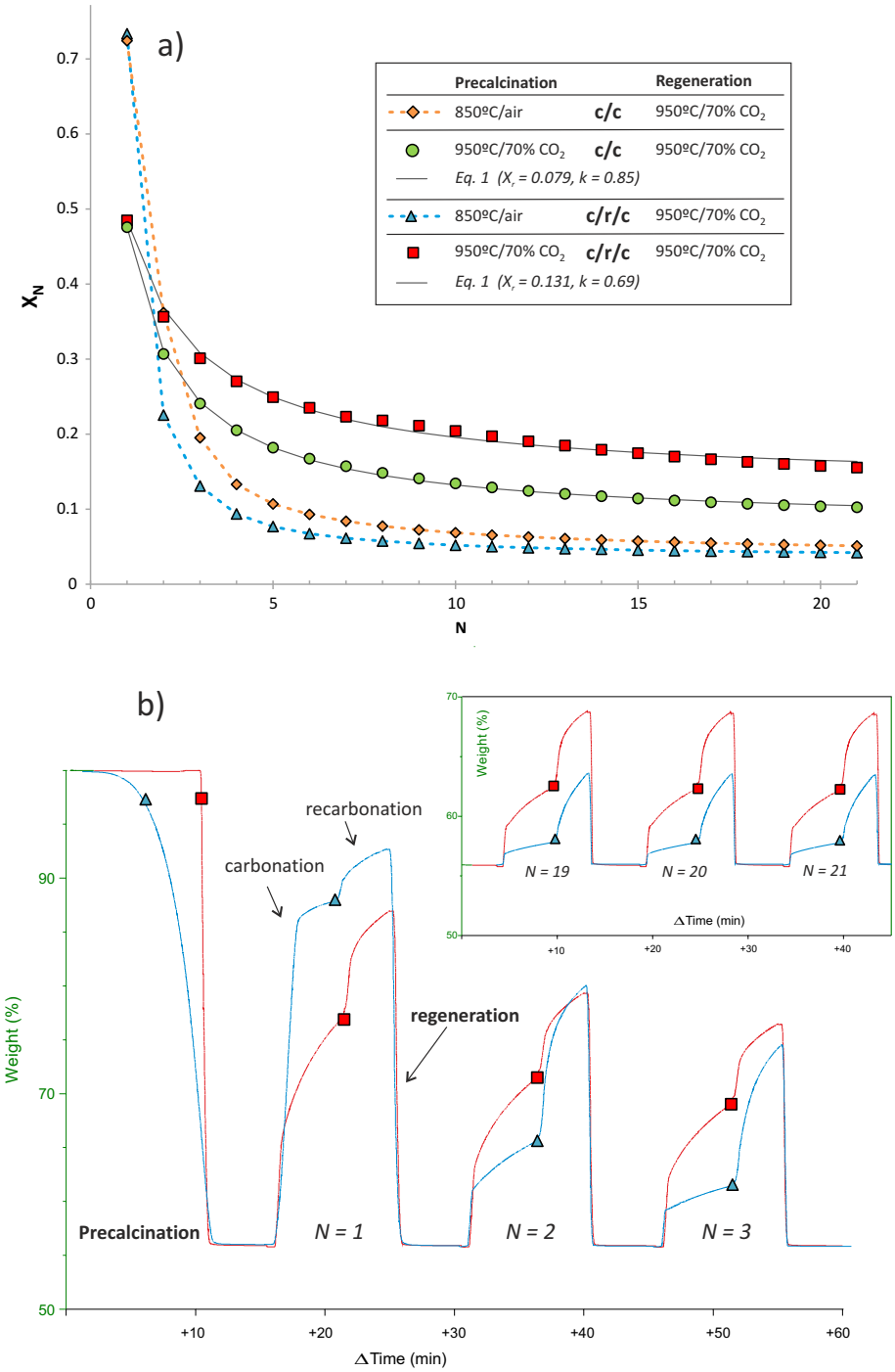


FIG. 3: a) CaO conversion at the end of the carbonation stage (X_N) as a function of the cycle number (N) for samples of raw limestone subjected to carbonation/calcination (c/c) and carbonation/recarbonation/calcination (c/r/c) cycles. Carbonation and calcination conditions as in Fig. 2. Recarbonation at 800°C for 3 min (90% CO_2/10% air vol/vol). Different precalcination conditions are indicated. The solid lines in a) are the best fits from Eq. 1. b) Time evolution of sorbent weight % during precalcination and the three first and last (inset) c/r/c cycles.

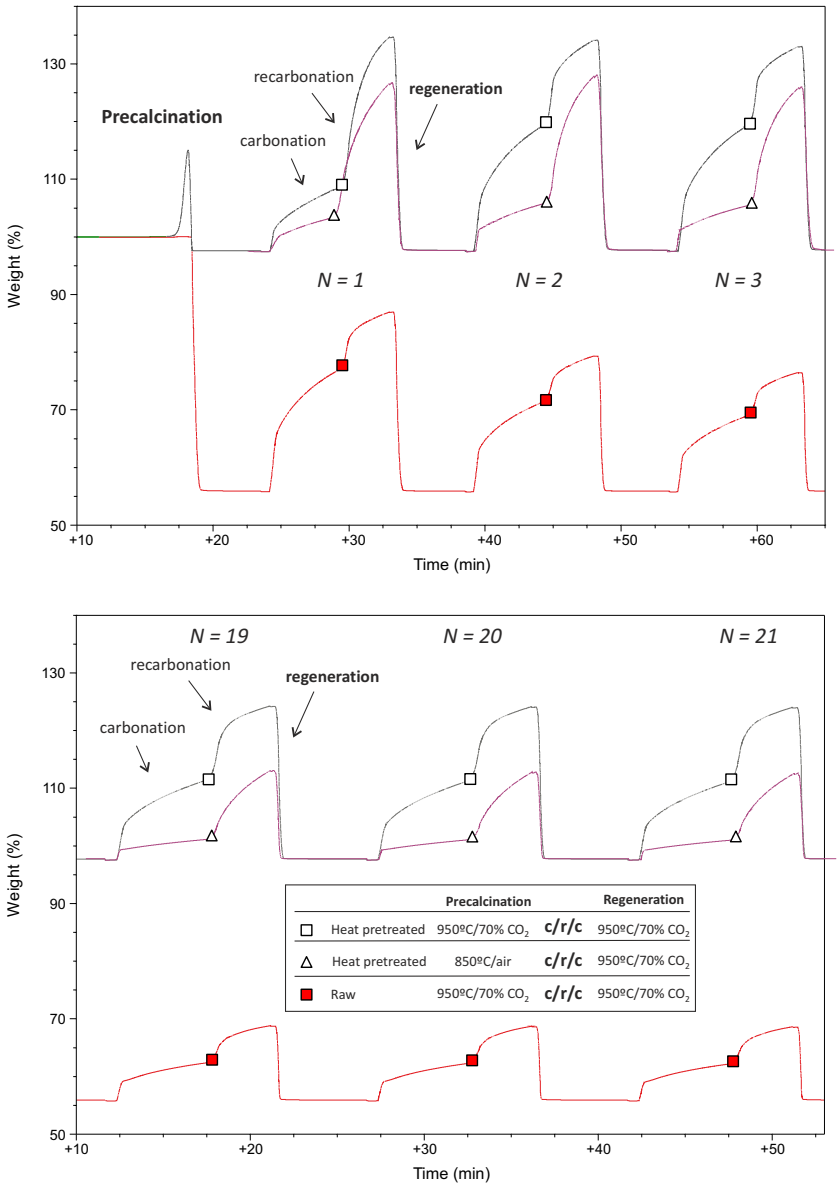


FIG. 4: Time evolution of sorbent weight % during precalcination and the first and last three carbonation/recarbonation/calcination (c/r/c) cycles for heat pretreated and raw limestone samples. Carbonation, recarbonation and calcination conditions as in Fig. 3. Different precalcination conditions are indicated.

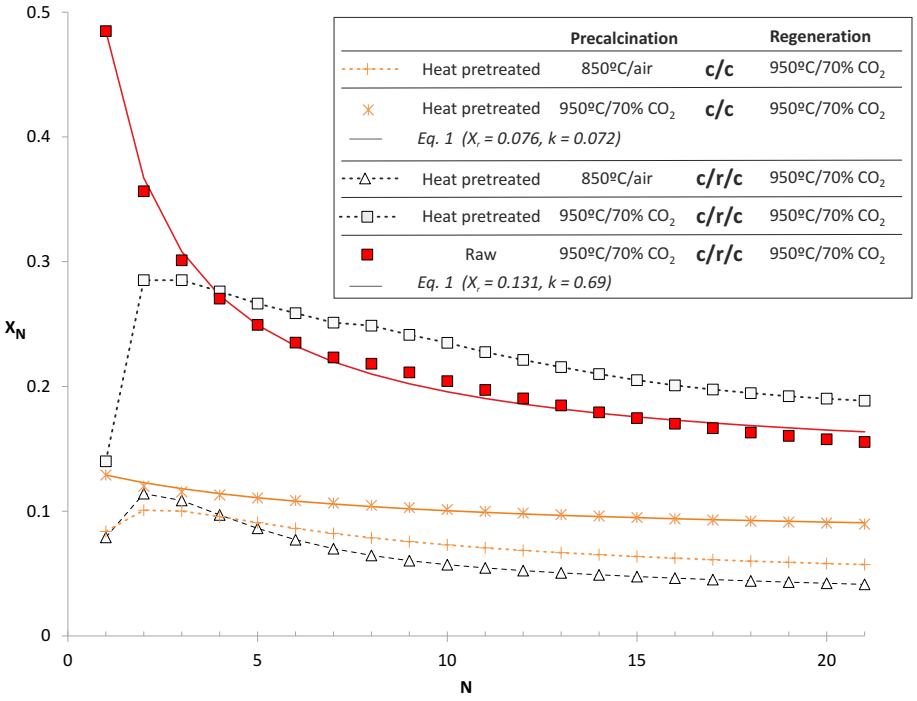


FIG. 5: CaO conversion at the end of the carbonation stage (X_N) as a function of the cycle number (N) for samples of heat pretreated and raw limestone subjected to carbonation/calcination (c/c) and carbonation/recarbonation/calcination (c/r/c) cycles. Carbonation, recarbonation and calcination conditions as in Fig. 3. Different precalcination conditions are indicated. The solid lines are the best fits from Eq. 1.

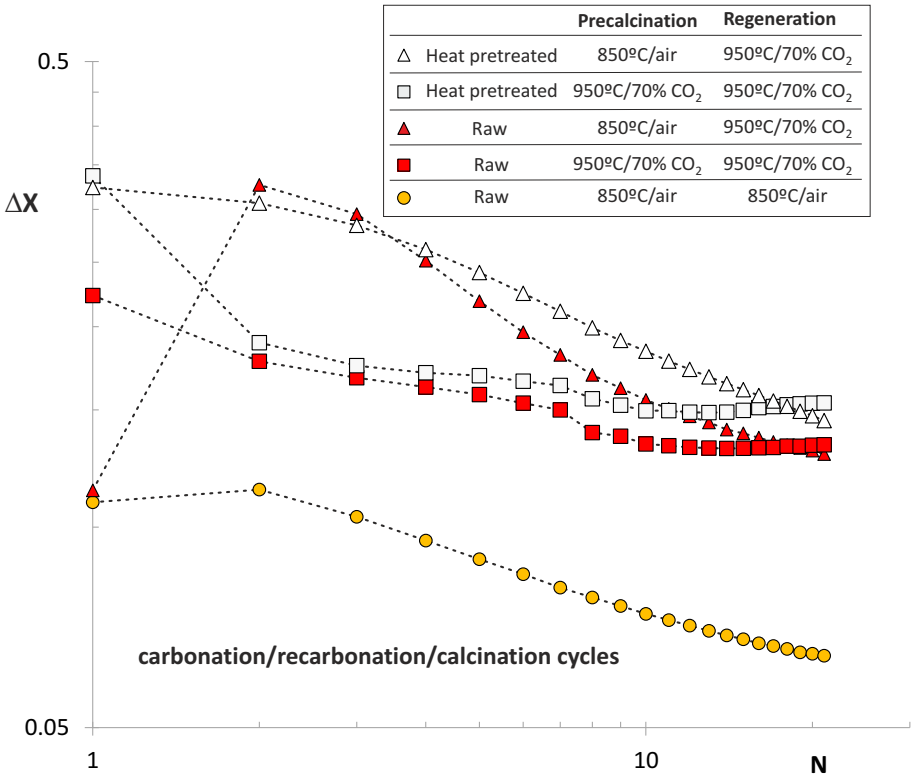


FIG. 6: CaO conversion in the recarbonation stage ΔX as a function of the cycle number N (log-log scale) for samples of heat pretreated and raw limestone subjected to carbonation/recarbonation/calcination (c/r/c) cycles. Carbonation, recarbonation and calcination conditions as in Fig. 3. Different precalcination conditions are indicated. Data from tests reported elsewhere [26] in which sorbent regeneration was carried out in air at 850°C are shown for comparison.

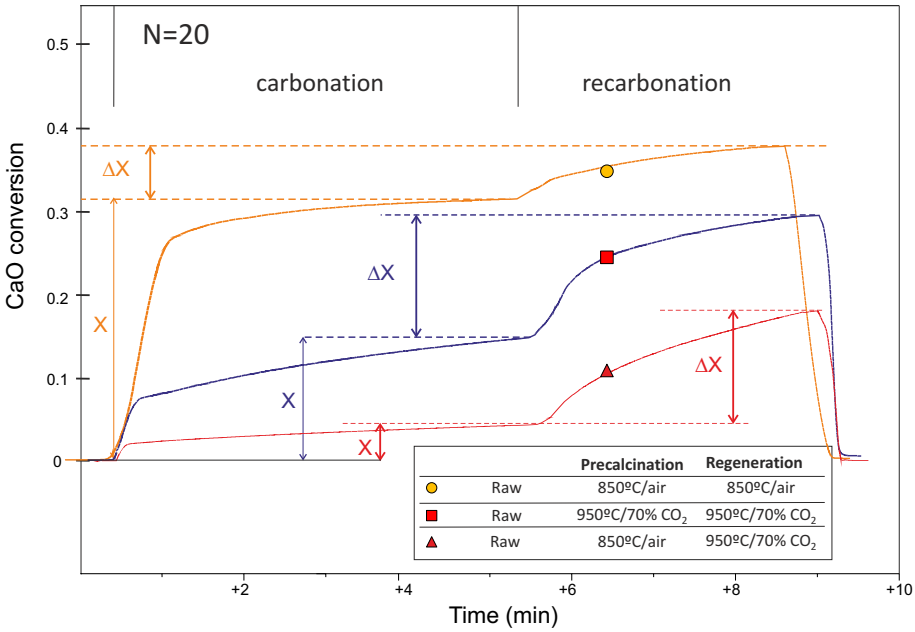


FIG. 7: Time evolution of CaO conversion in the 20th carbonation/recarbonation/calcination cycle for samples of raw limestone. Carbonation, recarbonation and calcination conditions as in Fig. 3. Different precalcination conditions are indicated.

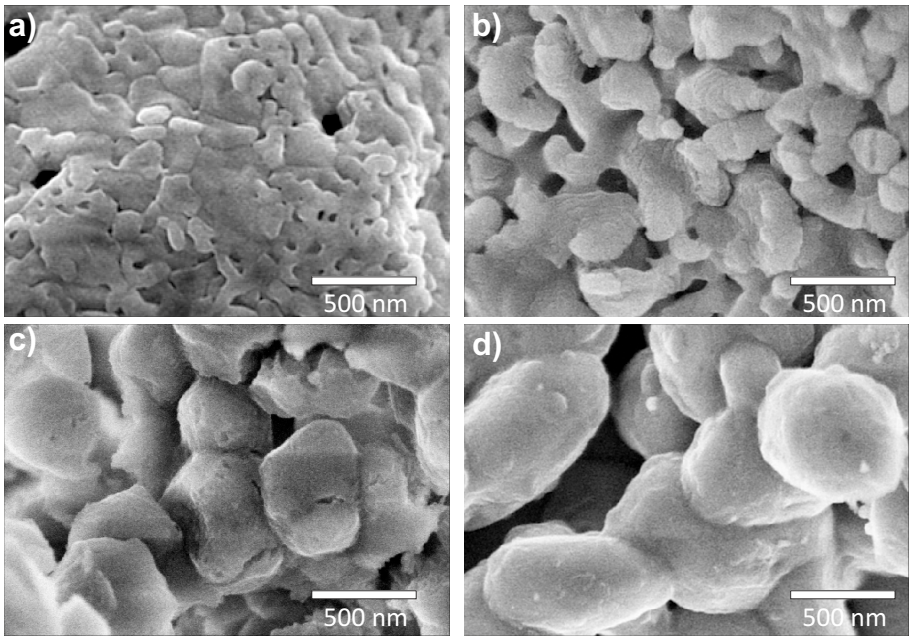
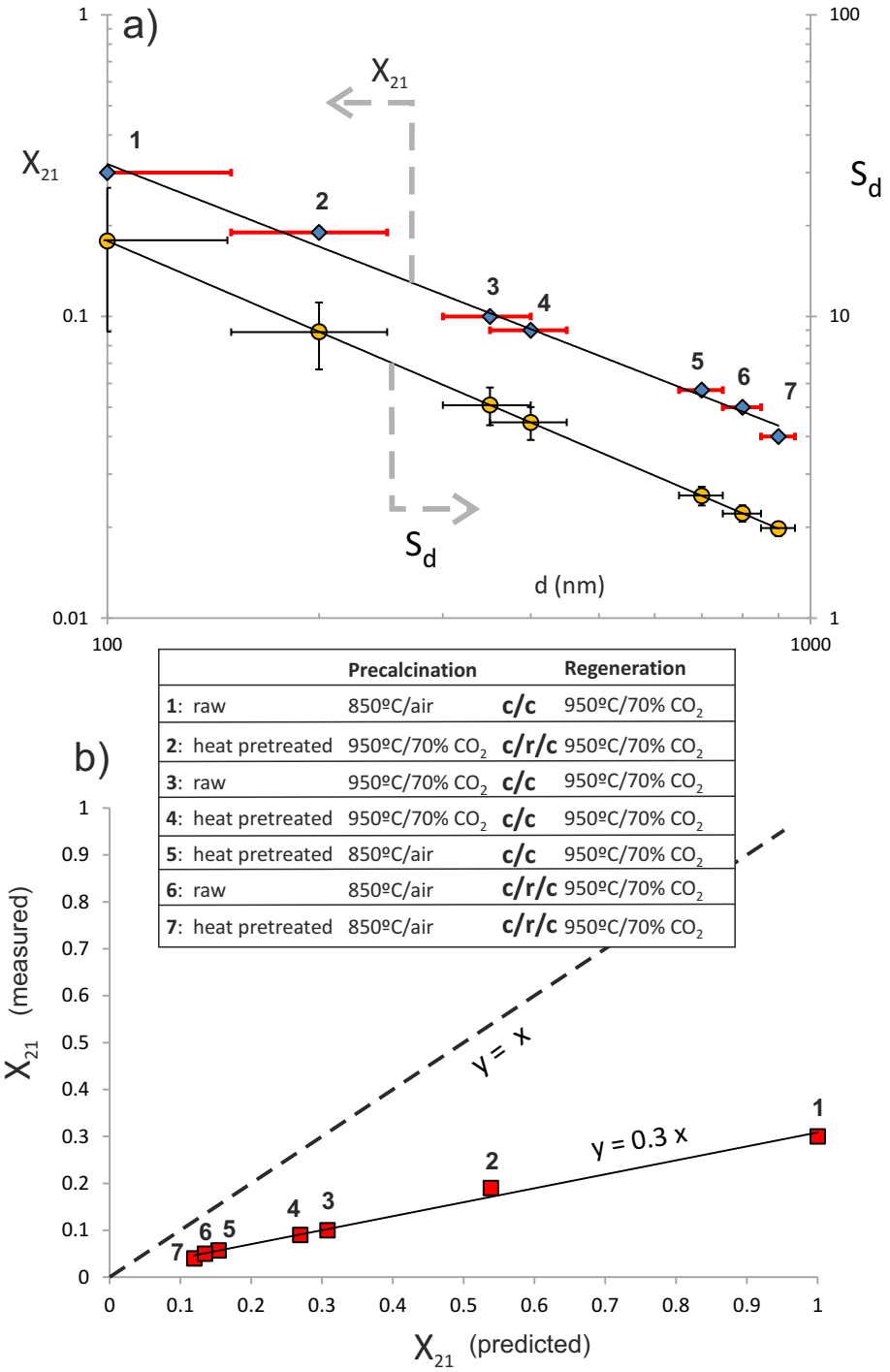


FIG. 8: SEM pictures of limestone samples after being subjected to 20 carbonation/recarbonation/calcination (a and b) and carbonation/calcination cycles (c and d). under different precalcination and regeneration (calcination) conditions. Carbonation and recarbonation conditions as in Fig. 3. a) Precalcination and calcination (regeneration) at 850°C in air (TGA tests reported in [26]). b) and c) Precalcination and calcination (regeneration) at 950°C in 70%CO_2/30% air vol/vol. d) Precalcination at 850°C in air and calcination (regeneration) at 950°C in 70%CO_2/30% air vol/vol.



	Precalcination		Regeneration
1: raw	850ºC/air	**c/c**	950ºC/70% CO_2
2: heat pretreated	950ºC/70% CO_2	**c/r/c**	950ºC/70% CO_2
3: raw	950ºC/70% CO_2	**c/c**	950ºC/70% CO_2
4: heat pretreated	950ºC/70% CO_2	**c/c**	950ºC/70% CO_2
5: heat pretreated	850ºC/air	**c/c**	950ºC/70% CO_2
6: raw	850ºC/air	**c/r/c**	950ºC/70% CO_2
7: heat pretreated	850ºC/air	**c/r/c**	950ºC/70% CO_2

FIG. 9: a) CaO conversion (left axis) measured at the 20th cycle X_{21} for the samples tested at diverse conditions (indicated) as a function of the grain size d estimated from the SEM images (the solid line is a power law fit $X_{21} \propto d^{-1}$). Values of the specific surface S_d are plotted using the right axis. b) X_{21} measured at the 20th cycle versus predicted from Eq. 2 using $S = S_d$ and $h = 40$ nm. Numerical labels indicate the conditions of the tests as detailed in the inset.

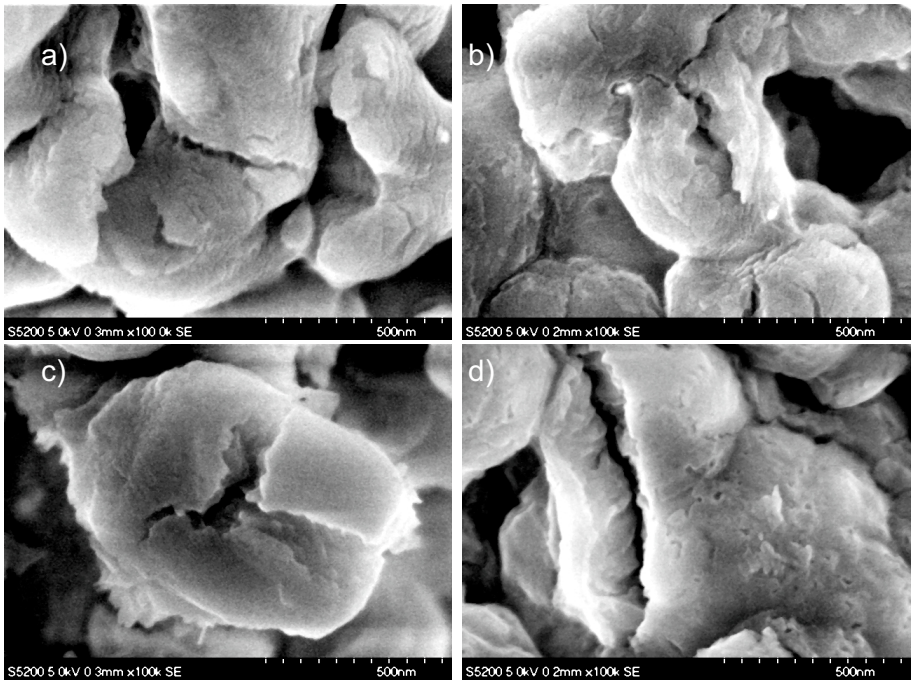


FIG. 10: SEM pictures of limestone samples after being subjected to 20 carbonation/recarbonation/calcination (a and b) and carbonation/calcination cycles (c and d) regenerated at 950°C in 70%CO_2/30% air vol/vol. Raw (a) and heat pretreated (b) samples precalcined at 850°C in air. Raw (c) and heat pretreated (d) samples precalcined at 950°C in 70%CO_2/30% air vol/vol.